Dechlorination comparison of mono-substituted PCBs with Mg/Pd in different solvent systems

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ARTICLE INFO

ABSTRACT

It is widely recognized that polychlorinated biphenyls (PCBs) are a dangerous environmental pollutant. Even though the use and production of PCBs have been restricted, heavy industrial use has made them a wide-spread environmental issue today. Dehalogenation using zero-valent metals has been a promising avenue of research for the remediation of chlorinated compounds and other contaminants that are present in the environment. However, zero-valent metals by themselves have shown little capability of dechlorinating polychlorinated biphenyls (PCBs). Mechanically alloying the metal with a catalyst, such as palladium, creates a bimetallic system capable of dechlorinating PCBs very rapidly to biphenyl. This study primarily aims to evaluate the effects of solvent specificity on the kinetics of mono-substituted PCBs, in an attempt to determine the mechanism of degradation. Rate constants and final byproducts were determined for the contaminant systems in both water and methanol, and significant differences in the relative rates of reaction were observed between the two solvents.

1. Introduction

Polychlorinated biphenyl (PCB) is an overarching term used to denote the family of 209 congeners having the generic formula $C_{12}H_nCl_{10-n}$. Before governmental regulation of PCB's in the 1970's, mixtures of multiple PCB congeners, commonly known as Arochlors, were used in a myriad of industrial applications because of their high boiling points, high degree of stability, low flammability, antifungal properties and low electrical conductivity. These applications included; use in transformers and capacitors as a dielectric fluid, heat transfer and hydraulic fluids, dye carriers in carbonless copy paper, paints, adhesives and caulking compounds, and fillers in investment casting wax (EPA, 1983). Over time many of the containers and/or compounds to which PCBs were added have themselves broken down allowing the highly stable PCBs to enter into the environment where they may be dispersed mainly through atmospheric transport (Eisenreich et al., 1983).

Reductive dechlorination is the primary means of PCB remediation. In this reaction chlorine atoms on the biphenyl are replaced (one at a time) by hydrogen atoms, producing a mixture of daughter products whose structure is determined by the position of the chlorine removed from the parent PCB. Although ideally the reductive dechlorination reactions will lead to the non-toxic, final product of biphenyl, each stepwise reaction is important since less chlorinated PCBs have been shown to be less toxic (Mousa et al., 1996; Quensen et al., 1998), have lower bioaccumulation factors, and are more susceptible to aerobic metabolism such as mineralization and ring opening (Bedard et al., 1987; Mousa et al., 1996). The most common remediation technique in use today is high temperature incineration; however, the costs associated with fuel and the production of highly toxic byproducts such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-furans (commonly referred to as dioxins) (Wu et al., 2005) which may result from incomplete incineration make this process less than ideal. Dredging and subsequent land filling of the contaminated soils and materials has also been used as a means of site decontamination, however, due to the highly stable nature of PCBs this technique merely displaces the point source of the PCB contamination. A third technique currently being investigated is microbial degradation but initial results show slow reaction rates and the inability of the microbes to completely dechlorinate PCBs (Erickson, 1992).

A preferable technique would be one which completely dechlorinates PCBs, could be applied *in situ*, and is low cost. To this end, much recent work has focused on the use of zero-valent metals such as magnesium, zinc and iron. Initial studies showed that zero-valent iron dechlorinated PCBs at temperatures above 200 °C (Chuang et al., 1995) and subsequent research has shown
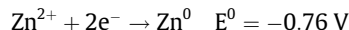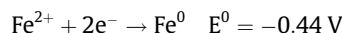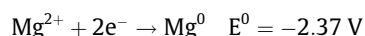
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that coating zero-valent iron with palladium, a known hydrode-halogenation catalyst (Kovenklioglu et al., 1992; Cheng et al., 1997; Wang and Zhang, 1997; Lowry and Reinhard, 1999; Li and Farrell, 2000), allows the dechlorination of various chlorinated organic compounds to proceed both at a faster rate and at ambient temperatures. Studies conducted by Muftikian et al. showed rapid dechlorination of tetrachlorinated ethene (PCE) using a palladium/iron (Pd/Fe) bimetal (Grittini et al., 1995; Muftkian et al., 1995) were one of the first groups to demonstrate the effectiveness of the Pd/Fe bimetal for the dechlorination of PCBs, however, they did not quantify their results (Grittini et al., 1995). In this same article, Grittini proposed that the greater reactivity seen with the addition of the palladium catalyst is due to the palladium's ability to adsorb molecular hydrogen generated from the reaction of iron and water

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

In the studies conducted for this paper, palladium is used as the hydrodehalogenation catalyst similar to the studies referred to thus far, however, magnesium was chosen as the zero-valent metal component of the bimetal for the following reasons. Unlike iron, magnesium forms a self-limiting oxide layer upon exposure to oxygen. This allows the Mg/Pd bimetal to be used in normal atmospheric conditions as opposed to the Fe/Pd bimetal which can only be used in an inert atmosphere environment. Secondly, magnesium provides a greater thermodynamic force when compared to other zero-valent metals such as iron and zinc:

$$Mg^{2+} + 2e^- \rightarrow Mg^0 \quad E^0 = -2.37 \text{ V}$$

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^0 = -0.44 \text{ V}$$

$$Zn^{2+} + 2e^- \rightarrow Zn^0 \quad E^0 = -0.76 \text{ V}$$

The studies discussed in this paper were designed for the purpose of elucidating the mechanism of PCB dechlorination since a fundamental mechanistic understanding of the reaction is vital to tailoring a bimetal system for maximum effectiveness. Because previous studies were conducted in water (Kim et al., 2004), the -ortho, -meta and -para (see Fig. 1) congeners of monochlorinated biphenyl were studied in both a water/methanol (9:1) mixture and pure methanol to determine solvent effects on the dechlorination mechanism. Additionally the final composition of the products was monitored to see if further degradation of the biphenyl product was occurring. Lastly, kinetic irregularities seen during approximately the first 30 min of PCB degradation studies conducted in methanol were investigated.
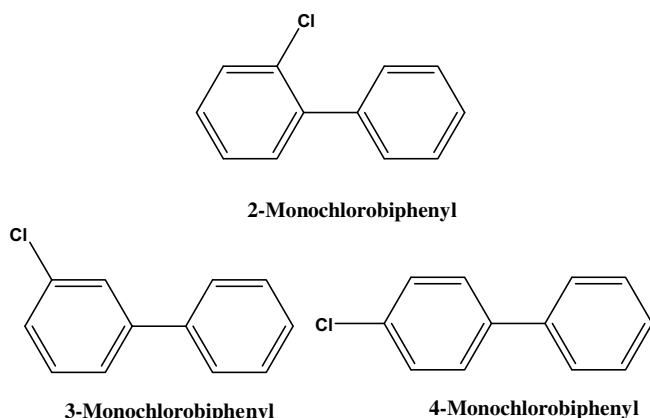

2-Monochlorobiphenyl

3-Monochlorobiphenyl　　　　**4-Monochlorobiphenyl**

Fig. 1. Structures of PCB-001, PCB-002, and PCB-003.

2. Experimental procedure

2.1. Materials and chemicals

Neat PCB standards were obtained from Accustandard and Optima® grade methanol and toluene were obtained from Fisher Scientific. About 99.0% Methanol-d was obtained from Acros Organics. Magnesium (~4 μm) was obtained from Hart Metals, Inc., and used as received. 1% palladium (on carbon) was obtained from Engelhard and was used as received. 10% palladium (on carbon) was obtained from Acros Organics and was used as received. An~0.08 wt% palladium–magnesium mixture was prepared by ball-milling 78 g Mg with 7 g of 1% palladium on carbon in a stainless steel canister (inner dimensions 5.5 cm by 17 cm) with a 16 steel ball bearings at a total mass of 261.15 g. The material was milled for 30 min using a Red Devil 5400 series paint mixer. An~0.8% wt% palladium–magnesium mixture was prepared in a similar fashion.

Solutions with 50 ugmL^{-1} concentration (in methanol) and 5 ugmL^{-1} (in 9:1 water:methanol) of PCB-001, PCB-002, and PCB-003, respectively, were prepared with corresponding calibration standards.

Experimental rate constants were normalized using a ρ constant (g of Mg/Pd per L of solution) to allow comparison between various studies.

2.2. Experimental procedure

Vial studies using 0.25 g of Mg/Pd and 10 mL of individual PCB solution in 20 mL vials (with PTFE lined caps) were conducted. Samples were placed on Cole-Parmer Series 57013 Reciprocating Shaker table (speed 7) until appropriate extraction time. Each extraction was performed as follows: Exactly, 10 mL of toluene was placed into the vial. The resulting mixture was then shaken by hand for 2 min. Next, 4 mL of this miscible solution was pulled with a glass syringe with a Millex® 0.45 μm nylon syringe filter attached and placed into a centrifuge tube with a PTFE lined cap (to prevent evaporation). The mixture was then shaken by hand for 2 min followed with centrifugation for 2 min. The top layer of the extract was collected for further analysis. Studies in 9:1 water:methanol were conducted similarly, however, the starting weight of Mg/Pd was 50 mg and after the 2 min of shaking, a 5 min ultrasound treatment was performed, to more fully extract the PCBs from the surface of the bimetal.

Analysis of the extracted samples were performed on a Shimadzu GC-2014 w/TOF MS and a Thermo Finnigan Trace GC/DSQ, both with a RTX-5 column containing 5% diphenyl-95% dimethyl polysiloxane with the temperature ramped from 120 °C to 270 °C. Identification of each of the monochlorinated PCBs was based upon the retention times of known standards.

3. Results and discussion

Zero-valent magnesium coated with 1% palladium on graphite showed 50% dechlorination of a 10 mL 50 ugmL^{-1} methanol solution of PCB-001 within 30 min and had a normalized pseudo-first order rate constant of $k = 0.0011$ L min^{-1} g^{-1}. The reaction with PCB-002 and PCB-003 with Mg/Pd showed 50% dechlorination slightly after 2 h and the normalized pseudo-first order rate constants of $k = 0.00045$ L min^{-1} g^{-1} and $k = 0.00052$ L min^{-1} g^{-1}, respectively. Pseudo-first order kinetics plots of each reaction are found in Fig. 2.

A similar set of experiments were conducted using a solvent system comprised of 90% water and 10% methanol (used to increase solubility). In these studies, 0.05 g of 1% Mg/Pd was used instead of 0.25 g, due to greater reactivity of the Mg/Pd in water. Also, the
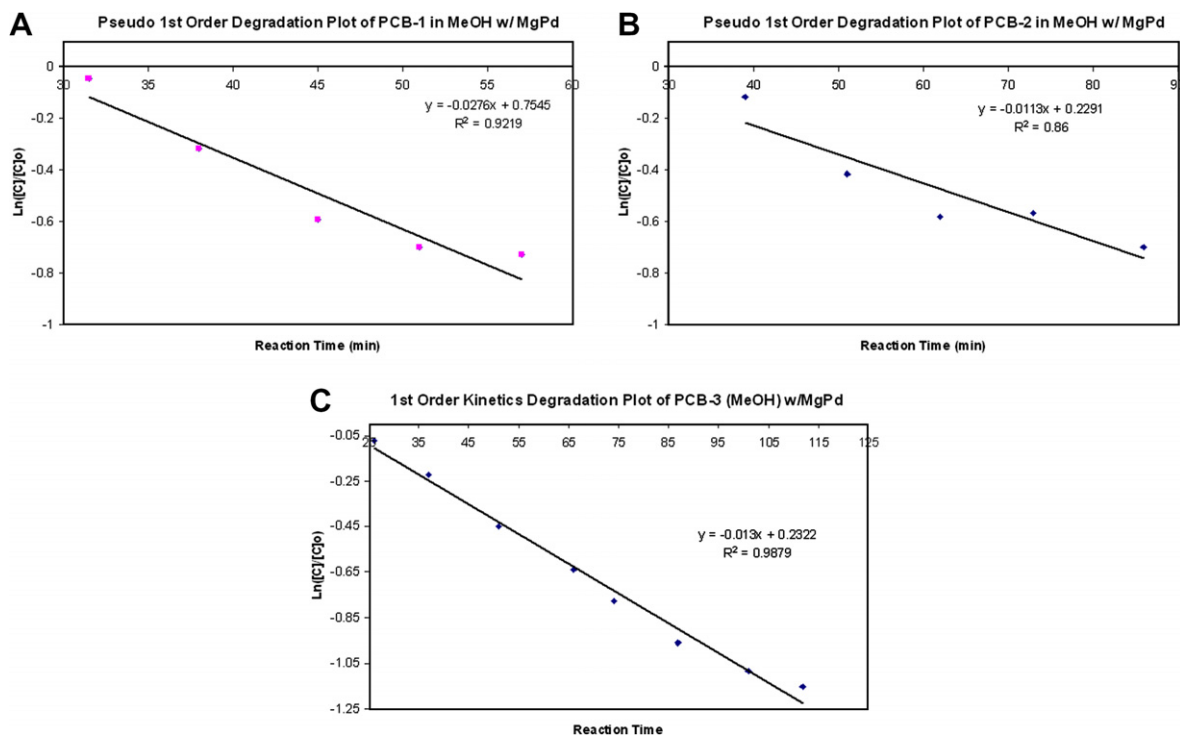
Fig. 2. Kinetic plot of degradation of (A) PCB-001, (B) PCB-002, and (C) PCB-003 with Mg/Pd in MeOH.

samples were exposed to a 5 min period of ultrasound to assist in extraction of any adsorbed PCBs from the surface of the catalytic metal prior to syringe filtering. Starting concentrations were also lower (5 ugmL^{-1}–10 ugmL^{-1}) due to solubility issues of PCBs in water. Pseudo-first order kinetic plots are shown in Fig. 3. Pseudo-first order rate constants obtained were $k = 0.00226$ L min^{-1} g^{-1}, $k = 0.00486$ L min^{-1} g^{-1}, and $k = 0.00716$ L min^{-1} g^{-1} for PCB-001, PCB-002, and PCB-003, respectively.

Kim et al. (2004) performed a similar study on monochlorinated biphenyls in water using Pd/Zn and Pd/Fe (16). They achieved results similar to what was observed in the experiments conducted in the water:methanol solvent system, but there were some differences when compared to the pure methanol system. Kim et al. observed that the rate of dechlorination for monochlorinated congeners in water was PCB-003 > PCB-002 > PCB-001, which is in agreement with the experimental results presented above. The
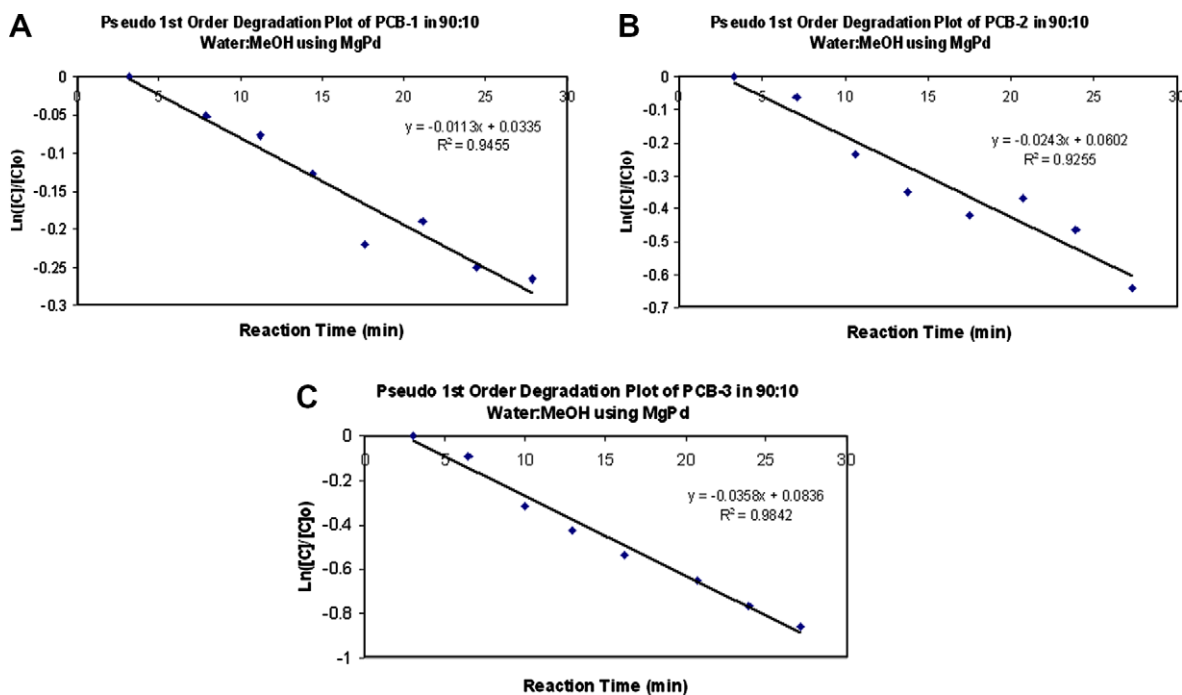

Fig. 3. Kinetic plot of degradation of (A) PCB-001, (B) PCB-002, and (C) PCB-003 with Mg/Pd in 90%/10% Water/Methanol.

studies conducted in pure methanol solvent show a completely different preference for dechlorination, PCB-001 > PCB-003 > PCB-002. The differences presented above could be due to a multitude of factors. In the methanol study, the reversal in the dechlorination trend may indicate that bimetallic degradation is dependent upon the proton donor that is used. In addition, the previous study used both Zn/Pd and Fe/Pd, rather than Mg/Pd, which may indicate different bimetallics can undergo different mechanistic pathways. Finally, the bimetallics were prepared differently which may also affect the mechanism of degradation. Kim et al. (2004) used electrodeposition to prepare the Zn/Pd and Fe/Pd, whereas the Mg/Pd was prepared by mechanically alloying.

One interesting data point that appeared in all three studies performed using methanol as the solvent system was that there appeared to an initial "lag time" before significant degradation would begin to occur. In all three of the monochlorinated studies performed in methanol that are presented in this paper, that lag time was approximately 30 min. Higher chlorinated congeners have exhibited similar "lag" times as well. One possible explanation for this is that it requires a certain amount of time for enough molecular/atomic hydrogen to be generated before degradation can occur. To test this theory, a study was initiated in which pure methanol and ~0.25 g of 1% Mg/Pd were allowed to react for ~30 min, at which point the samples were spiked with PCB-001 to a concentration consistent with prior studies. The samples were then extracted and analyzed as before. The data is included in Fig. 4.

This study produced a rate constant almost identical to previous study without the additional "lag" time. This indicates that the reason for the difference in kinetics is due to generation/adsorption of hydrogen rather than the adsorption of the contaminant itself, other wise the same ~30 min "lag" time would have been observed in this study. Interestingly enough, this trend is not seen in studies with water as the solvent, most likely due to water's greater ability
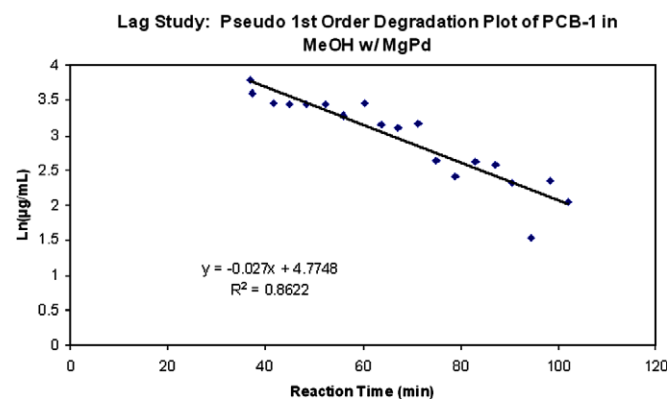

Fig. 4. First order kinetics plot of PCB-1 from "Lag" study.

to donate a proton, thus creating molecular hydrogen more quickly.

Another important question to answer is the final fate of the contaminant, whether or not biphenyl is the end product or is it degraded further. Studies were conducted in both methanol and 9:1 water:methanol solvent systems with more active palladized magnesium was used (10% Mg/Pd vs. 1% Mg/Pd) in order to answer this question. The results are shown below in Fig. 5. There is no significant degradation of biphenyl apparent with pure methanol as the solvent in more than 30 d. However, the studies with 9:1 water:methanol show significant degradation within the first 6 h, and near complete degradation within 3 d. This is in agreement with other published studies where the primary solvent is water (Kim et al., 2004).

The source of hydrogen in this reaction was investigated to determine if it was coming from the alcohol or methyl moiety of
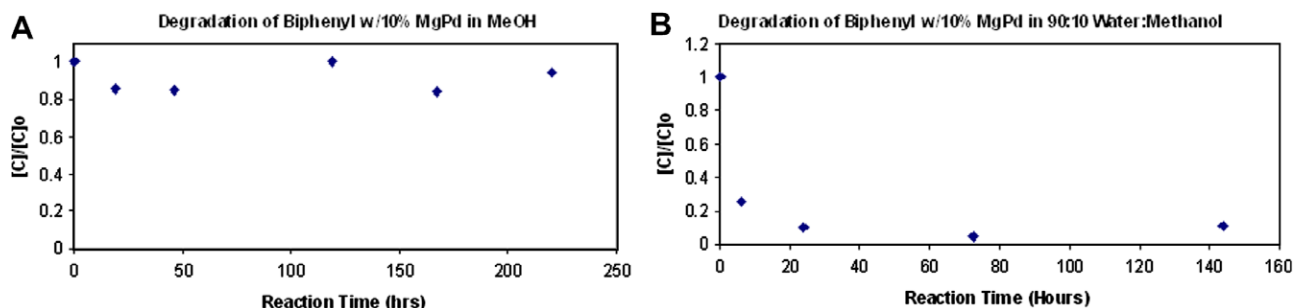

Fig. 5. Degradation of biphenyl in (A) methanol and (B) 90:10 water:methanol w/10% Mg/Pd.
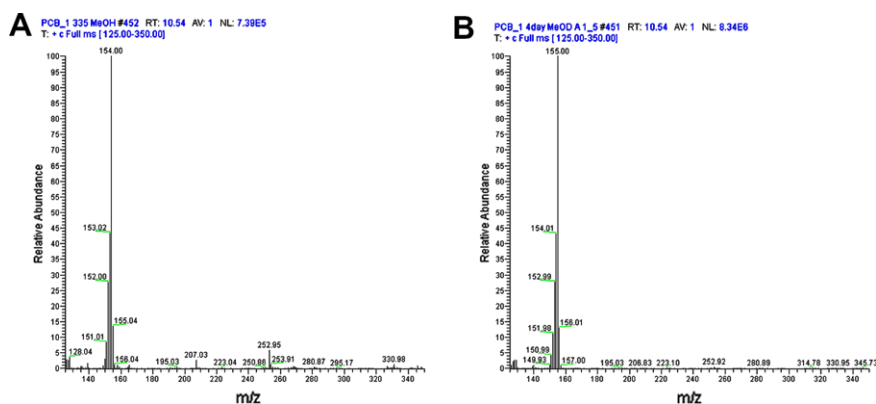

Fig. 6. Mass spectra of PCB-1 degraded with Mg/Pd in (A) MeOH and (B) MeOD.

the solvent. Gas-phase studies show that the methyl C–H bond requires less energy to break then the O–H bond in methanol (Blanksby and Ellison, 2003). However, whether or not this is true in this reaction is not clear, due to the role that solvent effects can play in bond strengths. In order to determine the source of the hydrogen, an isotopically labeled reaction study was performed using PCB-1. Methanol-D (CH$_3$OD) was used as the solvent, and the byproducts were determined by GC–MS. If the proton was coming from the alcohol group, then the m/z ratio of the biphenyl byproduct will be 1 amu higher than when the same study is run using pure methanol as the solvent. The mass spectra of both of these studies are given in Fig. 6. As can be seen in the corresponding mass spectra, when pure methanol is used as the reacting solvent, the parent ion of the biphenyl byproduct is 154 m/z. When isotopically labeled methanol-d is used, however, the parent ion of biphenyl is 155 m/z. This conclusively demonstrates that the proton being donated in the reaction is coming from the alcohol group of the methanol, rather than from the methyl group (as gas-phase data suggests). Additionally, this information rules out the possibility of the dechlorination going through a benzyne intermediate, which was being considered as a possible mechanistic pathway for Mg/Pd dechlorination. However, once the intermediate C–C triple bond is formed, two protons (or deuteriums) would have to add across the triple bond. The above data show only one additional deuterium was seen in the degradation of PCB-1 to biphenyl, eliminating the benzyne mechanism as a possible mechanistic pathway.

4. Conclusion

The research discussed above is highly indicative that the mechanism for degradation of polychlorinated biphenyls varies depending on the solvent system that is used. Previous research published indicates that the *para* substituted congener has the highest rate constant, followed by the *meta* and then the *ortho* monochlorinated congeners when performed in water solvent systems. Preliminary studies confirm this experimental observation with palladized magnesium when the experiments are performed in water:methanol (9:1), but when pure methanol is used as the solvent, the results are different. The order of increasing rate constants was found to be *ortho > para > meta* with pure methanol solvent systems. Additionally, studies performed in methanol do not begin degradation immediately (as is seen in the water:methanol studies). There is an initial period of no degradation, which seems to be due to the need for hydrogen to be created/adsorbed to the surface of the metal.

Mechanistically, it appears there may be solvent specificity as well. Not only are the relative rates of dechlorination different when comparing *ortho, meta,* and *para,* but the final byproducts also are different. In methanol systems, it does not appear that biphenyl is capable of being degraded any further. Conversely, in water:methanol systems, biphenyl is degraded in the presence of Mg/Pd. At this time, the final byproducts of that breakdown are not known. In both solvent systems, the proton being donated is

coming from hydrogen bound to oxygen (rather than coming from CH$_3$ in methanol). The exact mechanism of degradation using Mg/Pd is still not known at this time, but a benzyne intermediate has been eliminated as a possibility.

Acknowledgments

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